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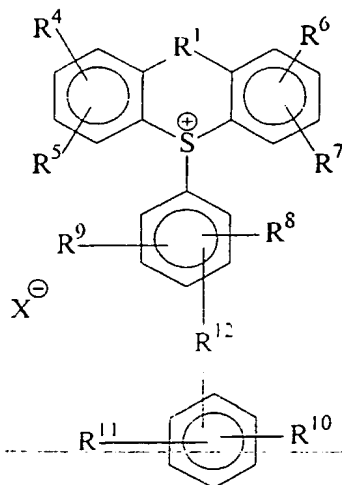
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(54) Title: NOVEL FUSED RING COMPOUNDS, AND THEIR USE AS CATIONIC PHOTOINITIATORS



(I)

(57) Abstract: Compounds of formula (I) [in which: R¹ represents a di-
rect bond, an oxygen atom, a group >CH₂, a sulphur atom, a group >C=O,
a group -(CH₂)₂- or a group of formula -N-R⁹, where R⁹ is hydrogen or an
alkyl; R⁴, R⁵, R⁶ and R⁷ are each hydrogen or various groups or atoms; R⁸,
R⁹, R¹⁰ and R¹¹ are each hydrogen, hydroxy, or alkyl; or R⁹ and R¹¹ form
a fused ring system with the benzene rings to which they are attached; R¹²
is a direct bond, oxygen atom or methylene; and X is an anion; and esters
thereof] are useful as cationic photoinitiators, especially for use in surface
coating applications, such as printing inks and varnishes, and which are
intended to be cured by polymerisation initiated by radiation.

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**NOVEL FUSED RING COMPOUNDS, AND THEIR USE AS CATIONIC
PHOTOINITIATORS**

The present invention relates to a series of novel fused ring, especially thioxanthone, 5 thianthrene, dibenzothiophene, thioxanthene, phenoxathiin or phenothiazine, compounds which are useful as cationic photoinitiators, especially for use in surface coating applications, such as printing inks and varnishes, and which are intended to be cured by polymerisation initiated by radiation.

Photocurable compositions are cured by exposure to radiation, usually ultraviolet radiation, and include for example, lacquers which may be applied to wood, metal or similar substrates by 10 suitable techniques such as roll coating or curtain coating. They may also be formulated as inks, for example to be applied by techniques such as letterpress, offset lithography, rotogravure printing, silk screen printing, inkjet or flexographic printing. Printing, depending on the particular printing technique, is applicable to a wide range of substrates which include paper, board, glass, plastics materials or metals. Other application areas will include adhesives, powder coatings, circuit boards 15 and microelectronic products, sterolithography, composites, optical fibres and liquid crystals.

Initiation of polymerisation in a monomer or prepolymer may be effected in a number of ways. One such way is by irradiation, for example with ultraviolet radiation, in which case it is normally necessary that the polymerisable composition should contain an initiator, commonly referred to as a "photoinitiator", or alternatively by an electron beam. There are two main types of curing chemistry 20 which can be used in this process; free radical and cationic. Although cationic curing has many advantages, its disadvantages, particularly with regard to the photoinitiators used, leads it to be used only in a minority of applications. Most frequently used cationic initiators are either organic iodonium or sulphonium salts.

Briefly, the mechanism by which a sulphonium cationic initiator acts when irradiated is that it 25 forms an excited state which then breaks down to release a radical cation. This radical cation reacts with the solvent, or another hydrogen atom donor, generating a protonic acid. The active species is the protonic acid. However, amongst the breakdown products of sulphonium salts are aromatic sulphides, such as diphenyl sulphide, which are malodorous and can be a health hazard, and lower aromatic hydrocarbons, such as benzene, which are potentially carcinogenic. Many of the commonly 30 used iodonium salts break down to give volatile species such as benzene, toluene or isobutyl benzene. This places severe restrictions upon the applications for which such cationic photoinitiators can be used. For example, they cannot be used in printing inks on packaging intended for food and, in some cases, cannot be used at all where the packaging is to be handled by the consumer. Indeed, as the industry becomes ever more conscious of health matters, it is increasingly difficult to use such 35 compounds at all.

However, this, although important, is not the only constraint upon the choice of compound to be used as a cationic photoinitiator. Even without consideration of the health issues, the cleavage products of the known cationic photoinitiators are malodorous, and it is highly desirable that unpleasant odours should be minimised. This leads to a desire that the cleavage products should be relatively non-volatile and non-odorous. The cationic photoinitiators must, of course, also be sufficiently stable, both as isolated compounds and when in the uncured coating formulation. They must also be soluble in or miscible with other components of the uncured coating formulation. Finally, they should be able to absorb radiation over a suitable and sufficiently wide range of wave lengths, ideally without the use of a sensitiser.

What is more, the nature of the cationic photoinitiator can have a major impact on the properties of the cured coating. The cationic photoinitiator should produce a coating which is fully cured, hard and resistant to common solvents and abuse.

Finally, there are a number of practical problems associated with the manufacture of the compounds used as cationic photoinitiators, including the necessity that they should be relatively easy and inexpensive to manufacture.

Thus, it would be desirable to provide a cationic photoinitiator which does not generate malodorous or toxic by-products upon radiation cure, particularly diphenyl sulphide and benzene, and which possesses the following properties: good solubility, good cure performance, good adhesion to substrates and reasonable cost.

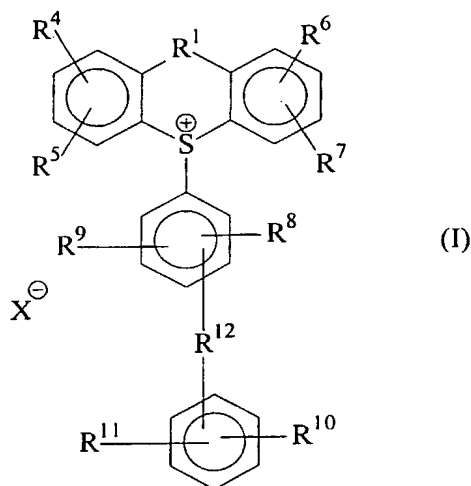
Not surprisingly, complying with all of these, often conflicting, requirements is not easy, and we are not aware of any completely satisfactory commercial solution available until now.

However, we have now discovered a series of new compounds, including thioxanthone derivatives, many of which have the advantages of good solubility in the coating composition combined with excellent cure. These compounds have a biphenyl or phenoxy- or benzyl-substituted phenyl group attached to the thioxanthone or analogous ring. In addition, the potential by-products of these new compounds would be thioxanthone derivatives typical of those used widely in free-radical curing inks for food packaging, and biphenyl, which is itself an approved antioxidant food additive in Europe.

Compounds of this general type are covered in general terms in US 4 161 478, although these lack the solubility of the compounds of the present invention, and the US Patent does not specifically disclose such compounds. Indeed, the US Patent is silent on the nature of the ring system attached to the thioxanthone or analogous ring system, although we have found that the nature of this ring system is highly important to the achievement of good solubility and cure. Also, a biphenyl-substituted dibenzothiophene compound is disclosed by Sato *et al.* [Phosphorus, Sulfur, and Silicon, 1994, Vol 95-96, pp 447-448], but no use is suggested for the resulting compounds. Similarly, a biphenyl-substituted thianthrene is disclosed by Kim and Kim (J. Heterocyclic Chem., 1998, Vol 35, pages

235-247), but this has only been prepared as a salt with a perchlorate anion, and no use is suggested for the compound other than in further synthetic chemistry.

Thus, the present invention consists in compounds of formula (I):



5 in which:

R^1 represents a direct bond, an oxygen atom, a group $>CH_2$, a sulphur atom, a group $>C=O$, a group $-(CH_2)_2-$ or a group of formula $-N-R^a$, where R^a represents a hydrogen atom or an alkyl group having from 1 to 12 carbon atoms;

R^4 , R^5 , R^6 and R^7 are individually the same or different and each represents a hydrogen atom or a group or atom selected from substituents α , defined below, provided that, when R^1 represents a group $>C=O$, then at least one of R^4 , R^5 , R^6 and R^7 represents a substituent α ;

R^8 , R^9 , R^{10} and R^{11} are individually the same or different and each represents a hydrogen atom, a hydroxy group, or an alkyl group having from 1 to 4 carbon atoms;

or R^9 and R^{11} are joined to form a fused ring system with the benzene rings to which they are attached;

R^{12} represents a direct bond, an oxygen atom or a methylene group;

said substituents α are: an alkyl group having from 1 to 20 carbon atoms, an alkoxy group having from 1 to 20 carbon atoms, an alkenyl group having from 2 to 20 carbon atoms, a halogen atom, a nitrile group, a hydroxyl group, an aryl group having from 6 to 10 carbon atoms, an aralkyl group having from 7 to 13 carbon atoms, an aryloxy group having from 6 to 10 carbon atoms, an aralkyloxy group having from 7 to 13 carbon atoms, an arylalkenyl group having from 8 to 12 carbon atoms, a cycloalkyl group having from 3 to 8 carbon atoms, a carboxy group, a carboxyalkoxy group having from 2 to 7 carbon atoms, an alkoxycarbonyl group having from 2 to 7 carbon atoms, an aryloxycarbonyl group having from 7 to 13 carbon atoms, an alkylcarbonyloxy group having from 2

to 7 carbon atoms, an alkanesulphonyl group having from 1 to 6 carbon atoms, an arenesulphonyl group having from 6 to 10 carbon atoms, an alkanoyl group having from 1 to 6 carbon atoms or an arylcarbonyl group having from 7 to 11 carbon atoms; and

X^- represents an anion, provided X^- does not represent an alkoxy, hydroxyalkoxy or aryloxy group when R^1 represents a direct bond; and esters thereof.

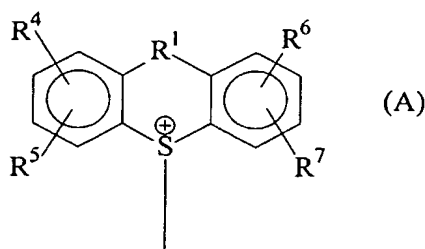
These compounds are useful as photoinitiators for use in energy, e.g. UV, curable coating compositions, including varnishes, lacquers and printing inks, most especially printing inks.

The compounds of the present invention may, as described above, be used as cationic photoinitiators for radiation-curable coating compositions. Thus, the present invention also provides an energy-curable composition comprising: (a) a polymerisable monomer, prepolymer or oligomer, especially a material which undergoes acid-catalysed ring opening polymerisation, e.g. an epoxide (oxirane) or oxetane, or an ethylenically unsaturated material, such as vinyl or propenyl ethers and (b) a cationic photoinitiator which is a compound of formula (I), as defined above, or an ester thereof.

The invention still further provides a process for preparing a cured polymeric composition by exposing a composition of the present invention to curing energy, preferably ultraviolet radiation.

In the compounds of the present invention, we prefer those compounds of formula (I) in which R^1 represents a group $>C=O$, a sulphur atom or a direct bond, and especially those in which R^1 represents a group $>C=O$.

More preferred are those compounds of formula (I) in which the residue of formula (A):



is a residue of substituted or unsubstituted thianthrene, dibenzothiophene, thioxanthone, thioxanthene, phenoxathiin or phenothiazine, especially those in which said residue is a substituted thioxanthone.

Where R^4 , R^5 , R^6 or R^7 represents an alkyl group having from 1 to 20, preferably from 1 to 10, more preferably from 1 to 6 and most preferably from 1 to 3, carbon atoms, this may be a straight or branched chain group, and examples of such groups include the methyl, ethyl, propyl, isopropyl, butyl, isobutyl, t-butyl, pentyl, isopentyl, neopentyl, 2-methylbutyl, 1-ethylpropyl, 4-methylpentyl, 3-methylpentyl, 2-methylpentyl, 1-methylpentyl, 3,3-dimethylbutyl, 2,2-dimethylbutyl, 1,1-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 2,3-dimethylbutyl, 2-ethylbutyl, hexyl, isohexyl,

heptyl, octyl, nonyl, decyl, dodecyl, tridecyl, pentadecyl, octadecyl, nonadecyl and icosyl groups, but preferably the methyl, ethyl, propyl, isopropyl and t-butyl groups, and most preferably the ethyl or isopropyl group. R^a may be any of the groups having from 1 to 12 carbon atoms exemplified above, especially those having from 1 to 6 carbon atoms, and preferably the methyl group.

5 Where R^4 , R^5 , R^6 or R^7 represents an alkoxy group having from 1 to 20, preferably from 1 to 10, more preferably from 1 to 6 and most preferably from 1 to 3, carbon atoms, this may be a straight or branched chain group, and examples of such groups include the methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, t-butoxy, pentyloxy, isopentyloxy, neopentyloxy, 2-methylbutoxy, 1-ethylpropoxy, 4-methylpentyloxy, 3-methylpentyloxy, 2-methylpentyloxy, 1-methylpentyloxy, 3,3-
10 dimethylbutoxy, 2,2-dimethylbutoxy, 1,1-dimethylbutoxy, 1,2-dimethylbutoxy, 1,3-dimethylbutoxy, 2,3-dimethylbutoxy, 2-ethylbutoxy, hexyloxy, isohexyloxy, heptyloxy, 2-ethylhexyloxy, octyloxy, nonyloxy, decyloxy, dodecyloxy, tridecyloxy, pentadecyloxy, octadecyloxy, nonadecyloxy and icosyloxy groups, but preferably the methoxy, ethoxy, t-butoxy and 2-ethylhexyloxy groups, and most preferably the 2-ethylhexyloxy group.

15 Where R^4 , R^5 , R^6 or R^7 represents an alkenyl group having from 2 to 20, preferably from 2 to 10, more preferably from 2 to 6 and most preferably from 2 to 4, carbon atoms, this may be a straight or branched chain group, and examples of such groups include the vinyl, 1-propenyl, allyl, isopropenyl, methallyl, butenyl, pentenyl, hexenyl, heptenyl, octenyl, nonenyl, decenyl, dodecenyl, tridecenyl, pentadecenyl, octadecenyl, nonadecenyl and icosenyl groups, but preferably the allyl,
20 methallyl and butenyl groups, and most preferably the allyl group.

Where R^4 , R^5 , R^6 or R^7 represents a halogen atom, this may be, for example, a fluorine, chlorine, bromine or iodine atom, preferably a chlorine atom.

Where R^4 , R^5 , R^6 or R^7 represents an aryl group, this has from 6 to 10 carbon atoms in one or more aromatic carbocyclic rings (which, if there are more than one, may be fused together). Such a
25 group may be substituted or unsubstituted, and, if substituted, the substituent(s) is preferably an alkyl or alkoxy group (as defined above), or an alkoxycarbonyl group (as defined below). Preferred aryl groups are the phenyl and naphthyl (1- or 2-) groups, the phenyl group being most preferred.

Where R^4 , R^5 , R^6 or R^7 represents an aryloxy group, this may be any of the aryl groups above bonded to an oxygen atom, and examples include the phenoxy and naphthyloxy groups.

30 Where R^4 , R^5 , R^6 or R^7 represents an aralkyl group, this is an alkyl group having from 1 to 4 carbon atoms which is substituted by one or two aryl groups as defined and exemplified above. Examples of such aralkyl groups include the benzyl, α -phenylethyl, β -phenylethyl, 3-phenylpropyl, 4-phenylbutyl, diphenylmethyl, 1-naphthylmethyl and 2-naphthylmethyl groups, of which the benzyl group is preferred.

Where R^4 , R^5 , R^6 or R^7 represents an aralkyloxy group, this may be any of the aralkyl groups above bonded to an oxygen atom, and examples include the benzyloxy, α -phenylethoxy, β -phenylethoxy, 3-phenylpropoxy, 4-phenylbutoxy, diphenylmethoxy, 1-naphthylmethoxy and 2-naphthylmethoxy groups, of which the benzyloxy group is preferred.

5 Where R^4 , R^5 , R^6 or R^7 represents an arylalkenyl group having from 8 to 12 carbon atoms, the aryl and alkenyl parts of this group may be as defined and exemplified above for the respective component parts. Specific examples of such groups are the styryl and cinnamyl groups.

10 Where R^4 , R^5 , R^6 or R^7 represents a cycloalkyl group having from 3 to 8 carbon atoms, this may be, for example, the cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl or cyclooctyl group.

Where R^4 , R^5 , R^6 or R^7 represents a carboxyalkoxy group, this may be any of the alkoxy groups having from 1 to 6 carbon atoms described above which is substituted by a carboxy group. Preferred examples include the carboxymethoxy, 2-carboxyethoxy and 4-carboxybutoxy groups, of which the carboxymethoxy group is preferred.

15 Where R^4 , R^5 , R^6 or R^7 represents an alkoxycarbonyl group, this has from 1 to 6 carbon atoms in the alkoxy part, and thus a total of from 2 to 7 carbon atoms. It may be a straight or branched chain group, and examples of such groups include the methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl, isopropoxycarbonyl, butoxycarbonyl, isobutoxycarbonyl, t-butoxycarbonyl, pentyloxycarbonyl, isopentyloxycarbonyl, neopentyloxycarbonyl, 2-methylbutoxycarbonyl, 1-ethylpropoxycarbonyl, 4-methylpentyloxycarbonyl, 3-methylpentyloxycarbonyl, 2-methylpentyloxycarbonyl, 1-methylpentyloxycarbonyl, 3,3-dimethylbutoxycarbonyl, 2,2-dimethylbutoxycarbonyl, 1,1-dimethylbutoxycarbonyl, 1,2-dimethylbutoxycarbonyl, 1,3-dimethylbutoxycarbonyl, 2,3-dimethylbutoxycarbonyl, 2-ethylbutoxycarbonyl, hexyloxycarbonyl and isohexyloxycarbonyl groups, but preferably the methoxycarbonyl, ethoxycarbonyl and t-butoxycarbonyl groups, and most preferably the methoxycarbonyl or ethoxycarbonyl group.

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Where R^4 , R^5 , R^6 or R^7 represents an aryloxycarbonyl group having from 7 to 13 carbon atoms, the aryl part of this may be any of the aryl groups defined and exemplified above. Specific examples of such groups include the phenoxycarbonyl and naphthyloxycarbonyl groups.

30 Where R^4 , R^5 , R^6 or R^7 represents an alkylcarbonyloxy group having from 2 to 7 carbon atoms, this may be any of the alkoxycarbonyl groups defined and exemplified above bonded to an oxygen atom.

Where R^4 , R^5 , R^6 or R^7 represents an alkanesulphonyl group, this has from 1 to 6 carbon atoms and is a straight or branched chain group. Examples of such groups include the methanesulphonyl, ethanesulphonyl, propanesulphonyl, isopropanesulphonyl, butanesulphonyl,

isobutanesulphonyl, t-butanesulphonyl, pentanesulphonyl and hexanesulphonyl groups, of which the methanesulphonyl group is preferred.

Where R^4 , R^5 , R^6 or R^7 represents an arenesulphonyl group, the aryl part may be as defined and exemplified above, and examples include the benzenesulphonyl and p-toluenesulphonyl groups.

5 Where R^4 , R^5 , R^6 or R^7 represents an alkanoyl group having from 1 to 6 carbon atoms, and preferably from 1 to 4 carbon atoms, this may be a straight or branched chain group, and examples include the formyl, acetyl, propionyl, butyryl, isobutyryl, pivaloyl, valeryl, isovaleryl, and hexanoyl groups, of which the acetyl group is most preferred;

10 Where R^4 , R^5 , R^6 or R^7 represents an arylcarbonyl group, the aryl part has from 6 to 10, more preferably 6 or 10, and most preferably 6, ring carbon atoms and is a carbocyclic group, which is unsubstituted or has from 1 to 5, preferably from 1 to 3 substituents, as defined and exemplified above. The preferred groups are the benzoyl and naphthoyl groups.

We particularly prefer those compounds of formula (I) in which R^4 , R^5 , R^6 and R^7 are individually the same or different and each represents a hydrogen atom, an alkyl group having from 1
15 to 10 carbon atoms, an alkoxy group having from 1 to 10 carbon atoms, a halogen atom, or a cycloalkyl group having from 3 to 8 carbon atoms, more especially those in which two or three of R^4 , R^5 , R^6 and R^7 represent hydrogen atoms, and most preferably those in which one or two of R^4 , R^5 , R^6 and R^7 represents an ethyl or isopropyl group. The most preferred compounds are those in which one or two of R^4 , R^5 , R^6 and R^7 represent ethyl groups or in which one of R^4 , R^5 , R^6 and R^7
20 represents an isopropyl group and the others represent hydrogen atoms.

Where R^8 , R^9 , R^{10} or R^{11} represents an alkyl group, this may be a straight or branched chain alkyl group having from 1 to 4 carbon atoms, and examples include the methyl, ethyl, propyl, isopropyl, butyl, isobutyl and t-butyl groups, of which the methyl group is preferred.

We prefer those compounds of formula (I) in which two, three or four of R^8 , R^9 , R^{10} and R^{11}
25 represent hydrogen atoms, and especially those in which all of R^8 , R^9 , R^{10} and R^{11} represent hydrogen atoms.

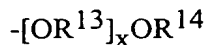
When R^9 and R^{11} , together with the benzene rings to which they are attached, form a fused ring system, this may be, for example, a biphenylene, fluorene or phenanthrene system, preferably fluorene.

30 R^{12} may be a direct bond (so that the two groups joined by R^{12} together form a biphenyl group), an oxygen atom (so that the two groups joined by R^{12} together form a phenoxyphenyl group), or a methylene group (so that the two groups joined by R^{12} together form a benzylphenyl group).

X^- represents an anion. In general, there is no particular limitation on the nature of the anion to be used. However, where the compounds of the present invention are to be used as photoinitiators, the anion should be non-nucleophilic, or essentially non-nucleophilic, as is well known in the art. It should also be relatively bulky. If the compounds are not to be used as photoinitiators, the anion need not meet these requirements. For example, in some cases, it may be desirable not to store the compound in the form of the salt which is ultimately to be used. In that case, it may be preferable to form another salt, and then convert the compound to the desired salt at or close to the point of use. In such a case, it is not necessary that the anion should be non-nucleophilic.

Examples of non-nucleophilic anions are well known to those skilled in the art, and include anions of formula MZ_n^- where M represents a phosphorus, boron, antimony, arsenic, chlorine or carbon atom, Z represents a halogen atom except where M represents a halogen atom, an oxygen atom or a sulphite group, and n is an integer dependent upon the valence of M and Z. Preferred examples of such groups include the PF_6^- , SbF_6^- , AsF_6^- , BF_4^- , $B(C_6F_5)_4^-$, $R^aB(Ph)_3^-$ (where R^a represents an alkyl group having from 1 to 6 carbon atoms and Ph represents a phenyl group), $R^bSO_3^-$ (where R^b represents an alkyl or haloalkyl group having from 1 to 6 carbon atoms or an aryl group), ClO_4^- and $ArSO_3^-$ (where Ar represents an aryl group) groups, of which the PF_6^- , SbF_6^- , AsF_6^- , $CF_3SO_3^-$ and BF_4^- groups are preferred and the PF_6^- group is most preferred.

Where the compounds of the present invention contain a carboxy group, i.e. where R^4 , R^5 , R^6 or R^7 represents a carboxy or carboxyalkoxy group, the resulting compounds may form esters, and these esters also form a part of the present invention. There is no particular limitation on the nature of the ester, other than those constraints well known to those skilled in the art, and preferred examples of esters include the alkyl esters, particularly those having from 1 to 12 carbon atoms, such as those containing the C_1 - C_{12} alkyl groups, and those derived from a polyalkylene glycol ether ester (especially the C_1 - C_4 alkyl ethers), such as esters containing groups of formula:



where R^{13} represents an alkylene group having from 1 to 8 carbon atoms, R^{14} represents an alkyl group having from 1 to 4 carbon atoms, and x is a number from 2 to 20, preferably from 5 to 10. More preferred are groups of formula:



where R^{14} and x are as defined above and R^{15} represents an alkyl group having from 1 to 4 carbon atoms.

Where R^8 , R^9 , R^{10} or R^{11} represents a hydroxy group, the resulting compounds may also form esters with acids. Examples of such esters are given in "Protective Groups in Organic Synthesis" by T. W. Greene and P. G. M. Wuts, Second Edition, 1991, published by John Wiley & Sons, Inc.

Any combination of the preferred substituent groups and atoms listed above in respect of R^1 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , is also envisaged by the present invention.

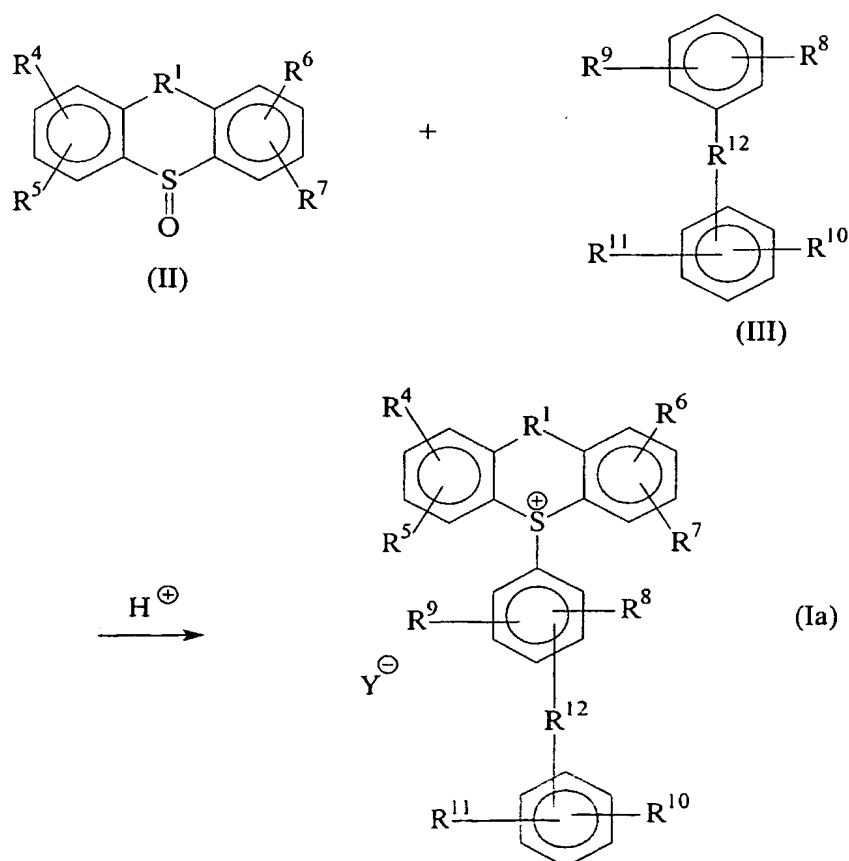
Particularly preferred compounds of the present invention having an especially good combination of good cure and good solubility in coating compositions are those compounds of formula (I) in which:

R^4 , R^5 , R^6 and R^7 are individually the same or different and each represents a hydrogen atom or an alkyl group having from 1 to 4 carbon atoms;

R^{12} represents a direct bond; and

R^8 , R^9 , R^{10} and R^{11} represent hydrogen atoms.

The compounds of the present invention may be prepared by reacting a sulfoxide corresponding to ring system (A) with the compound corresponding to the biphenyl, phenoxyphenyl or benzylphenyl ring system in the presence of an acid, as shown in the following scheme:



In the above formulae, R^1 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} and R^{11} are as defined above, and Y^- represents an anion, which will normally be derived from the reaction. Where any one or more of R^8 , R^9 , R^{10} , or R^{11} represents a hydroxy group, this is preferably protected, since it otherwise may react with the acid used in the reaction. The nature of the protecting group used is not critical to the invention, and any protecting group known in the art for use in compounds of this type may equally be used here. Examples of suitable protecting groups are described in "Protective Groups in Organic Synthesis" by T. W. Greene and P. G. M. Wuts, Second Edition, 1991, published by John Wiley & Sons, Inc.

The reaction is normally and preferably effected in a solvent, the nature of which is not critical, provided that it has no adverse effect on the reagents or on the reaction and provided that it can dissolve the reagents, at least to some extent. A suitable solvent is acetic acid.

The reaction is also preferably effected in the presence of a strong acid. Preferred is a combination of concentrated sulphuric acid and acetic anhydride.

A suitable reaction temperature is preferably below 15°C .

The sulphoxide of formula (II) may be prepared by well known methods.

Using the reaction scheme above, it is possible to obtain yields in excess of 90% in each reaction step, which assists the economics of the process.

In general, the anion Y^- will not be the anion X^- which it is desired to incorporate in the final product. If so, then the desired anion may be introduced by an anion exchange reaction, as is well known in the field of synthetic chemistry.

Where a protected hydroxy group represented by R^8 , R^9 , R^{10} , or R^{11} is present, the protecting group may, if desired, be removed by methods well known to those skilled in the art, as described in "Protective Groups in Organic Synthesis" above.

The compounds of the invention may then be separated from the reaction mixture by well known techniques and, if desired, further purified.

The composition of the present invention may be formulated as a printing ink, varnish, adhesive or any other coating composition which is intended to be cured by irradiation, whether by ultraviolet or electron beam. Such compositions will normally contain at least a polymerisable monomer, prepolymer or oligomer, and the cationic photoinitiator of the present invention, but may also include other components well known to those skilled in the art, for example, reactive diluents and, in the case of printing inks, a pigment.

A wide variety of monomers and prepolymers may be subjected to cationic photoinitiation using the compounds of the present invention as photoinitiators, and the nature of the monomers and prepolymers is not critical to the present invention. Such monomers and prepolymers typically contain cationically polymerisable groups, and general examples of such compounds include the

epoxides, oxetanes, other cyclic ethers, vinyl compounds (such as vinyl and propenyl ethers, styrene and its derivatives and unsaturated polyesters), unsaturated hydrocarbons, lactones and, in the case of hybrid systems, acrylates and methacrylates.

Typical epoxides which may be used include the cycloaliphatic epoxides (such as those sold under the designations UVR6110 by Union Carbide or UVACURE 1500 by UCB), which are well known to those skilled in the art.

Other epoxy-functional oligomers/monomers which may be used include the glycidyl ethers of polyols [bisphenol A, alkyl diols or poly(alkylene oxides), which be di-, tri-, tetra- or hexa-functional]. Also, epoxides derived by the epoxidation of unsaturated materials may also be used (e.g. epoxidised soybean oil, epoxidised polybutadiene or epoxidised alkenes). Naturally occurring epoxides may also be used, including the crop oil collected from Vernonia galamensis.

As well as epoxides, other reactive monomers/oligomers which may be used include the vinyl ethers of polyols [such as triethylene glycol divinyl ether, 1,4-cyclohexane dimethanol divinyl ether and the vinyl ethers of poly(alkylene oxides)]. Examples of vinyl ether functional prepolymers include the urethane-based products supplied by Allied Signal. Similarly, monomers/oligomers containing propenyl ether groups may be used in place of the corresponding compounds referred to above containing vinyl ether groups.

Similarly, compounds bearing oxetane groups may be used in place of the corresponding compounds referred to above containing epoxide groups. A typical oxetane is that derived from trimethylolpropane (3-ethyl-3-hydroxymethyloxetane).

Other reactive species can include styrene derivatives and cyclic esters (such as lactones and their derivatives).

It is also common to include polyols in ultraviolet cationic curable formulations, which promote the cross-linking by a chain-transfer process. Examples of polyols include the ethoxylated/propoxylated derivatives of, for example, trimethylolpropane, pentaerythritol, di-trimethylolpropane, di-pentaerythritol and sorbitan esters, as well as more conventional poly(ethylene oxide)s and poly(propylene oxide)s. Other polyols well known to those skilled in the art are the polycaprolactone diols, triols and tetraols, such as those supplied by Union Carbide.

Additives which may be used in conjunction with the principal components of the coating formulations of the present invention include stabilisers, plasticisers, pigments, waxes, slip aids, levelling aids, adhesion promoters, surfactants and fillers. Also, compounds which act as sensitisers for the photoinitiator, such as thioxanthone (and derivatives), benzophenone (and derivatives), hydroxyalkylphenones, anthracene (and derivatives), perylene, xanthone, pyrene and anthraquinone, may be included.

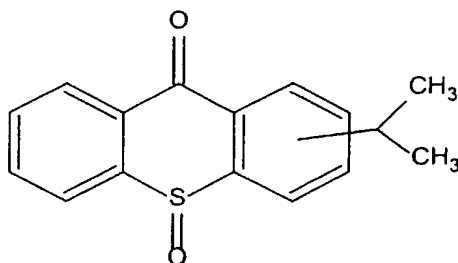
The compounds of the present invention may be included as photoinitiators in coating formulations such are well known in the art, and the precise composition of such formulations will

vary depending upon the other components and the intended use, as is well known. However, a typical formulation for an ink coatable by flexography might be:

Pigment	8 - 20%
Photoinitiator	2 - 6%
Monomer/prepolymer/oligomer	30 - 90%
Polyol	0 - 30%
Additives	0 - 10%

5 In order to enhance the solubility of the compounds of the present invention in the curable composition, they may first be dissolved in a suitable solvent, for example propylene carbonate.

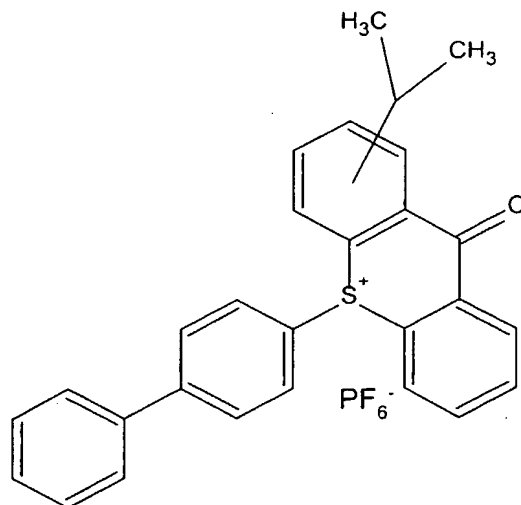
The invention is further illustrated by the following non-limiting Examples.

EXAMPLE 1**5 Preparation of isopropylthioxanthone sulphoxide**

10 10.0g of ITX (isopropylthioxanthone) (0.03937moles) were dissolved in 630ml of a mixture of acetonitrile and water (75% acetonitrile, 25% water). Gentle heating was required to dissolve the isopropylthioxanthone (35°C). 86.34g of Ceric ammonium nitrate (0.15748moles) were added in one batch. The reaction was followed by thin layer chromatography (TLC). The reaction mixture was then stirred for 1 hour at room temperature. 400ml of water was then added and the mixture was
15 extracted with 1000ml of diethyl ether. The ether layers were combined and dried with magnesium sulphate, and the ether was removed on a rotary evaporator to yield the product.

Product yield 9.92g (93.32%) of a yellow solid.

The product was analysed by HPLC, LC-MS and IR

EXAMPLE 2

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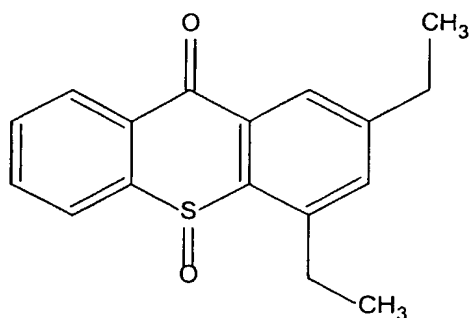
2.025g (0.0075moles) of the compound of Example 1, biphenyl (1.604g, 0.01040moles), acetic acid (7ml), dichloromethane (1.75ml) and acetic anhydride (7ml) were mixed in round bottomed flask. The temperature of the mixture was reduced to <15°C using a water/ice bath. Concentrated sulphuric acid (2.6ml) was then added drop wise, making sure the temperature did not exceed 15°C. After the addition was complete, the mixture was stirred for 2 hours, allowing the temperature to increase to room temperature. 100ml of water was then added to the mixture. This was then extracted with ~200ml (2x100ml) of dichloromethane. The dichloromethane was then removed on a rotary evaporator. This yielded 7.17g of intermediate product. This was dissolved in a minimum of acetic acid. The solution was then poured into a KPF₆ solution (4g in 130ml water). This appeared to yield a viscous liquid. This was extracted with dichloromethane. The dichloromethane layer was then dried with magnesium sulphate, and the solvent was removed on a rotary evaporator to yield the product. A second extraction was also carried out by dissolving the product in dichloromethane and extracting with water, re-drying the dichloromethane and removing the dichloromethane using a rotary evaporator.

20

Product yield 4.12g (99.5%) of a brown pasty solid.

The product was analysed by HPLC, LC-MS and IR

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EXAMPLE 3

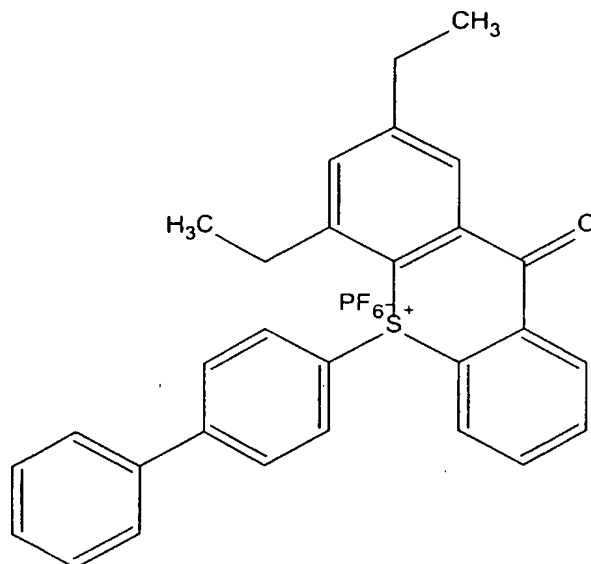
5

10.0g (0.03731moles) of 2,4-diethylthioxanthone (DETX) were dissolved in 630ml of a mixture of acetonitrile and water (75% acetonitrile, 25% water). Gentle heating was required to dissolve the DETX (45°C). 81.79g of Ceric ammonium nitrate (0.1492moles) were added in one batch. The reaction was followed by TLC. The reaction mixture was stirred for 45minutes. At this stage TLC indicated that the reaction was complete. The reaction mixture was allowed to cool to room temperature and 400ml of water was then added. The mixture was extracted with 1000ml of diethyl ether. The ether layers were combined and dried with magnesium sulphate, and the ether was removed on a rotary evaporator to yield the product. At this stage the product still contained some inorganic residue. The product was therefore re-dissolved in diethyl ether, washed with water and dried with magnesium sulphate. The ether was then removed on a rotary evaporator to yield the product.

20

Product is a yellow solid, yield not recorded.

The product was analysed by HPLC, LC-MS and IR.

EXAMPLE 4

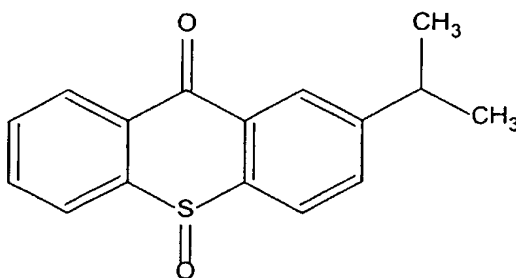
5

2.0g (0.00704moles), DETX sulfoxide from Example 3, biphenyl (1.503g, 0.0098moles), acetic acid (7ml), dichloromethane (1.75ml) and acetic anhydride (7ml) were mixed in round bottomed flask. The temperature of the mixture was reduced to <15°C using a water/ice bath. Concentrated sulphuric acid (2.6ml) was then added drop wise, making sure the temperature did not exceed 15°C. After the addition was complete, the mixture was stirred for 2 hours, allowing the temperature to increase to room temperature. 100ml of water was then added to the mixture. This was then extracted with ~200ml (2x100ml) of dichloromethane. The dichloromethane was then dried with magnesium sulphate, filtered and removed on a rotary evaporator. This yielded ~4.0g of intermediate product. This was dissolved in a minimum of acetic acid. The solution was then poured into a KPF₆ solution (2g in 65ml water). This appeared to yield a viscous liquid. This was extracted with dichloromethane. The dichloromethane layer was washed with 3x100ml water and then dried with magnesium sulphate, and the solvent was removed on a rotary evaporator to yield the product.

Product yield 2.12g (53.2%) of a brown pasty solid.

The product was analysed by HPLC, LC-MS and IR.

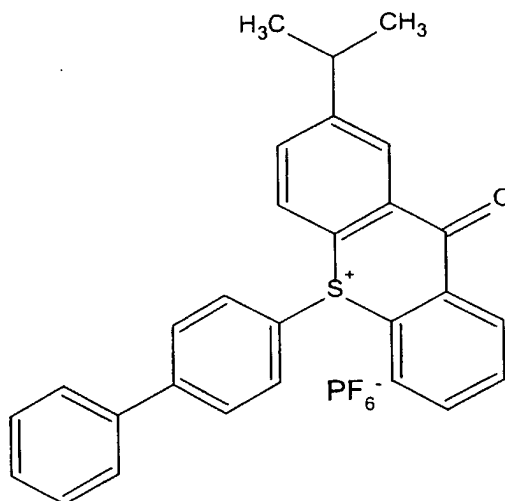
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EXAMPLE 5**5 Preparation of 2-isopropylthioxanthone sulphoxide**

10.0g (0.03937moles) of 2-isopropylthioxanthone were dissolved in 630ml of a mixture of
10 acetonitrile and water (75% acetonitrile, 25% water). Gentle heating was required to dissolve the 2-
isopropylthioxanthone (35°C). The temperature was then allowed to return to room temperature.
86.336g of Ceric ammonium nitrate (0.15748moles) were added in one batch. The reaction was
followed by TLC. The reaction mixture was stirred for 2.5 hours at room temperature. 400ml of
15 water was then added and the mixture was extracted with 1000ml of diethyl ether. The ether layers
were combined and dried with magnesium sulphate, and the ether was removed on a rotary evaporator
to yield the product. At this stage the product still contained some inorganic residue. The product
was therefore re-dissolved in diethyl ether, washed with water and dried with magnesium sulphate.
The ether was then removed on a rotary evaporator to yield the product.

Product yield 5.54g (52.3%) of a yellow solid.

20 The product was analysed by HPLC, LC-MS and IR

EXAMPLE 6

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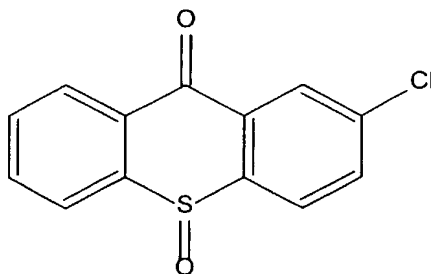
2.025g 2-isopropylthioxanthone sulfoxide (0.0075moles) from Example 5, biphenyl (1.604g, 0.01040moles), acetic acid (7ml), dichloromethane (1.75ml) and acetic anhydride (7ml) were mixed in a round bottomed flask. The temperature of the mixture was reduced to $<15^\circ\text{C}$ using a water/ice bath. Concentrated sulphuric acid (2.6ml) was then added drop wise, making sure the temperature did not exceed 15°C . After the addition was complete, the mixture was stirred for 2 hours, allowing the temperature to increase to room temperature. 100ml of water was then added to the mixture. This was then extracted with ~200ml (2x100ml) of dichloromethane. The dichloromethane was then dried with magnesium sulphate, filtered and removed on a rotary evaporator. This yielded 4.0g of intermediate product. This was dissolved in a minimum of acetic acid. The solution was then poured into a KPF_6 solution (2g in 65ml water). This appeared to yield a viscous liquid. This was extracted with dichloromethane. The dichloromethane layer was then dried with magnesium sulphate and the solvent was removed on a rotary evaporator to yield the product. There was still an odour of acetic acid. Therefore the product was dissolved in dichloromethane (100ml), and rewashed with 3x100ml water. The dichloromethane was dried with magnesium sulphate and filtered, and then the dichloromethane was removed on a rotary evaporator to yield the product.

20

Product yield 2.54g (61.2%) of a brown pasty solid.

The product was analysed by HPLC, LC-MS and IR.

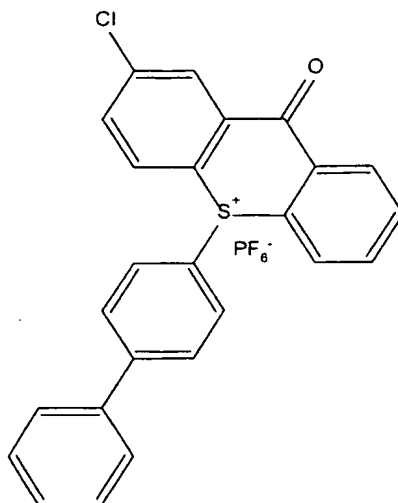
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EXAMPLE 7

9.71g of 2-chlorothioxanthone (0.03937moles) were dissolved in 630ml of a mixture of acetonitrile and water (75% acetonitrile, 25% water). A further 75ml of acetonitrile and heating was required to try to dissolve the 2-chlorothioxanthone (65°C). However, the 2-chlorothioxanthone was still not soluble but the reaction was carried out anyway. 86.336g of Ceric ammonium nitrate (0.15748moles) were added in one batch. The reaction was followed by TLC. The reaction mixture was stirred for 90mins at 65°C. 400ml of water was then added which crystallised the product. The product was collected by filtration and dried in a vacuum oven.

Product yield 6.96g (67.3%) of a yellow solid.

The product was analysed by HPLC, LC-MS and IR.

EXAMPLE 8

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1.97g 2-Chlorothioxanthone sulfoxide (0.0075moles) from Example 7, biphenyl (1.604g, 0.01040moles), acetic acid (7ml), dichloromethane (1.75ml) and acetic anhydride (7ml) were mixed in a round bottomed flask. The temperature of the mixture was reduced to <15°C using a water/ice bath.

10 Concentrated sulphuric acid (2.6ml) was then added drop wise, making sure the temperature did not exceed 15°C. After the addition was complete, the mixture was stirred for 2 hours, allowing the temperature to increase to room temperature. 100ml of water was then added to the mixture. This was then extracted with ~200ml (2x100ml) of dichloromethane. The dichloromethane was then removed on a rotary evaporator. This yielded 5.39g of intermediate product. This was dissolved in a

15 minimum of acetic acid. The solution was then poured into a KPF₆ solution (2.5g in 75ml water). This appeared to yield a viscous liquid. This was extracted with dichloromethane. The dichloromethane layer was then dried with magnesium sulphate and the solvent was removed on a rotary evaporator to yield the product.

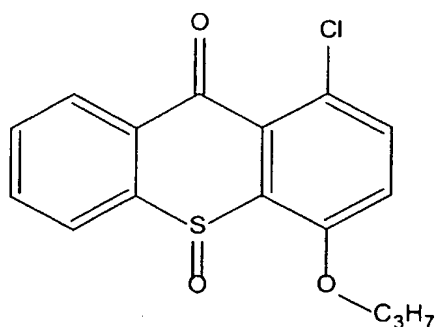
Product yield 3.42g (83.71%) of a brown pasty solid.

20

The product was analysed by HPLC, LC-MS and IR.

EXAMPLE 9

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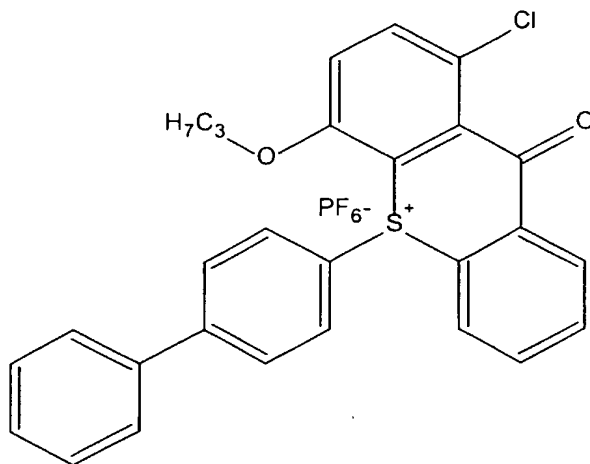
10.0g (0.0328moles) of 1-chloro-4-propoxythioxanthone (CPTX) were dissolved in 630ml of a mixture of acetonitrile and water (75% acetonitrile, 25% water). Gentle heating was required to dissolve the CPTX (50°C). 71.93g of Ceric ammonium nitrate (0.1312moles) were added in one batch. The reaction was followed by TLC. The reaction mixture was stirred for 1 hour. At this stage TLC indicated that the reaction was complete. The reaction was allowed to cool to room temperature and 400ml of water added. A small amount of precipitate formed. The mixture was extracted with 1000ml of diethyl ether. The ether solution was dried with magnesium sulphate, and the ether was removed on a rotary evaporator to yield the product that was subsequently dried in a vacuum oven.

Product yield 6.74g (72.7%) of a yellow / orange solid.

The product was analysed by HPLC, LC-MS and IR.

EXAMPLE 10

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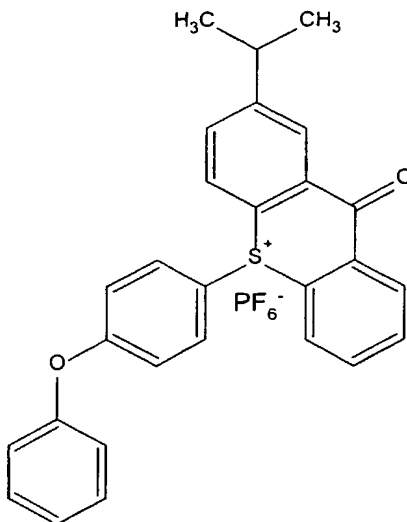
2.4g (0.0075moles) of CPTX sulfoxide from Example 9, biphenyl (1.6g, 0.0104moles), acetic acid (7ml), dichloromethane (1.75ml) and acetic anhydride (7ml) were mixed in a round bottomed flask. The temperature of the mixture was reduced to $<15^{\circ}\text{C}$ using a water/ice bath. Concentrated sulphuric acid (2.6ml) was then added drop wise, making sure the temperature did not exceed 15°C . After the addition was complete, the mixture was stirred for 2 hours, allowing the temperature to increase to room temperature. 100ml of water was then added to the mixture. This was then extracted with $\sim 200\text{ml}$ ($2 \times 100\text{ml}$) of dichloromethane. The dichloromethane was then dried with magnesium sulphate and filtered, and the solvent was removed on a rotary evaporator. This yielded $\sim 4.0\text{g}$ of intermediate product. This was dissolved in a minimum of acetic acid. The solution was then poured into a KPF_6 solution (2g in 65ml water). A viscous residue was obtained which was extracted into dichloromethane. The dichloromethane layer was washed with water ($3 \times 100\text{ml}$) and dried with magnesium sulphate, and then the dichloromethane was removed on a rotary evaporator to yield the product. The product is a dark brown viscous material which becomes more crystalline on standing.

Product yield 2.4g (44.3%) of a brown pasty solid.

The product was analysed by HPLC, LC-MS and IR.

EXAMPLE 11

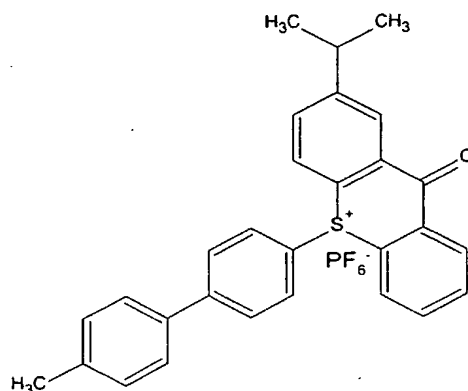
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(2.025g, 0.0075moles), 2-isopropylthioxanthone sulphoxide from Example 5, diphenyl ether (1.768g, 0.01040moles), acetic acid (7ml), dichloromethane (1.75ml) and acetic anhydride (7ml) were mixed in a round bottomed flask. The temperature of the mixture was reduced to <15°C using a water/ice bath. Concentrated sulphuric acid (2.6ml) was then added drop wise, making sure the temperature did not exceed 15°C. After the addition was complete, the mixture was stirred for 2 hours, allowing the temperature to increase to room temperature. 100ml of water was then added to the mixture. This was then extracted with ~200ml (2x100ml) of dichloromethane. The dichloromethane was then removed on a rotary evaporator. This yielded 6.21g of intermediate product. This was dissolved in a minimum of acetic acid. The solution was then poured into a KPF₆ solution (2.6g in 85ml water). This appeared to yield a viscous liquid. This was extracted with dichloromethane. The dichloromethane layer was then dried with magnesium sulphate and the solvent was removed on a rotary evaporator to yield the product.

20 Product yield 4.23g (99.3%) of an orange pasty solid.

The product was analysed by HPLC, LC-MS and IR.

EXAMPLE 12

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(2.025g, 0.0075moles), 2-isopropylthioxanthone sulfoxide from Example 5, 4-methyl biphenyl (1.75g, 0.01040moles), acetic acid (7ml), dichloromethane (1.75ml) and acetic anhydride (7ml) were mixed in a round bottomed flask. The temperature of the mixture was reduced to <15°C using a water/ice bath. Concentrated sulphuric acid (2.6ml) was then added drop wise, making sure the temperature did not exceed 15°C. After the addition was complete, the mixture was stirred for 2 hours, allowing the temperature to increase to room temperature. 100ml of water was then added to the mixture. This was then extracted with ~200ml (2x100ml) of dichloromethane. The dichloromethane was then removed on a rotary evaporator. This yielded 5.21g of intermediate product. This was dissolved in a minimum of acetic acid. The solution was then poured into a KPF₆ solution (2.5g in 75ml water). This appeared to yield a viscous liquid. This was extracted with dichloromethane. The dichloromethane layer was then dried with magnesium sulphate and the was solvent removed on a rotary evaporator to yield the product.

15

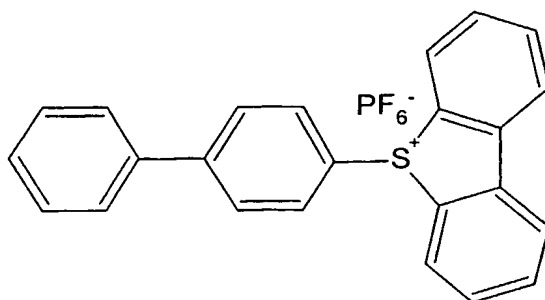
Product yield 2.69g (63.4%) of a brown pasty solid.

20

The product was analysed by HPLC, LC-MS and IR.

EXAMPLE 13

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1.5g Dibenzothiophene sulphoxide (0.0075moles), biphenyl (1.604g, 0.01040moles), acetic acid (7ml), dichloromethane (1.75ml) and acetic anhydride (7ml) were mixed in a round bottomed flask. The temperature of the mixture was reduced to <15°C using a water/ice bath. Concentrated sulphuric acid (2.6ml) was then added drop wise, making sure the temperature did not exceed 15°C. After the addition was complete, the mixture was stirred for 2 hours, allowing the temperature to increase to room temperature. 100ml of water was then added to the mixture. This was then extracted with ~200ml (2x100ml) of dichloromethane. The dichloromethane was then removed on a rotary evaporator. This yielded 4.41g of intermediate product. This was dissolved in a minimum of acetic acid. The solution was then poured into a KPF₆ solution (2.5g in 75ml water). The product crystallised from solution and was collected by filtration, washed with water and dried in a vacuum oven.

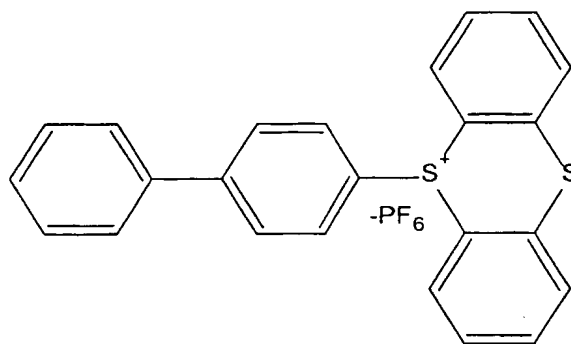
Product yield 3.04g (84.1%) of a light brown solid.

20

The product was analysed by HPLC, LC-MS and IR.

EXAMPLE 14

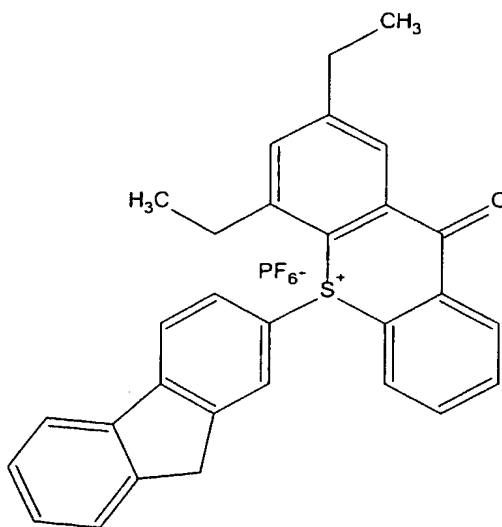
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Thianthrene sulphoxide (2.0g, 0.0086moles), biphenyl (1.86g, 0.012moles), acetic acid (7ml), dichloromethane (1.75ml) and acetic anhydride (7ml) were mixed in a round bottomed flask. A further 5ml of dichloromethane was added to dissolve the thianthrene sulphoxide. The temperature of the mixture was reduced to $<15^{\circ}C$ using a water/ice bath. Concentrated sulphuric acid (2.6ml) was then added drop wise, making sure the temperature did not exceed $15^{\circ}C$. After the addition was complete, the mixture was stirred for 2 hours, allowing the temperature to increase to room temperature. 100ml of water was then added to the mixture. This was then extracted with ~200ml (2x100ml) of dichloromethane. The dichloromethane was then dried with magnesium sulphate, filtered and removed on a rotary evaporator. This yielded 4.0g of intermediate product. This was dissolved in a minimum of acetic acid. The solution was then poured into a KPF_6 solution (2g in 65ml water). The product produced was a solid that was collected by filtration and washed with water. Finally, the product was dried in a vacuum oven.

Product yield 3.42g (77.1%) of a very pale pink solid.

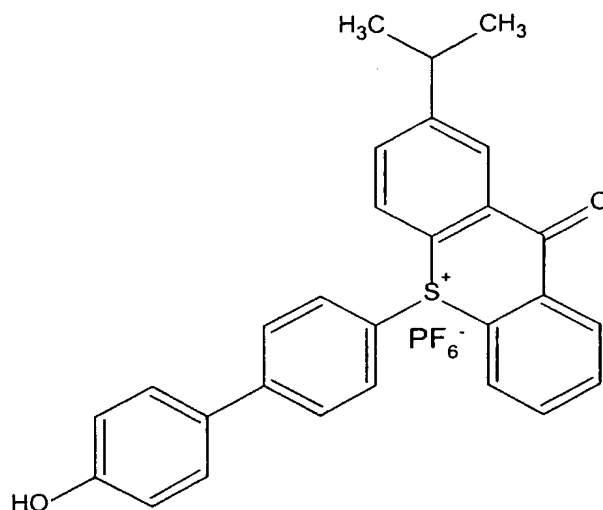
The product was analysed by HPLC, LC-MS and IR.

EXAMPLE 15

2.0g (0.00704moles), 2,4-diethylthioxanthone sulphoxide from Example 3, fluorene (1.63g, 0.0098moles), acetic acid (7ml), dichloromethane (1.75ml) and acetic anhydride (7ml) were mixed in a round bottomed flask. The temperature of the mixture was reduced to <15°C using a water/ice bath. Concentrated sulphuric acid (2.6ml) was then added drop wise, making sure the temperature did not exceed 15°C. After the addition was complete, the mixture was stirred for 2 hours, allowing the temperature to increase to room temperature. 100ml of water was then added to the mixture. This was then extracted with ~200ml (2x100ml) of dichloromethane. The dichloromethane was then dried with magnesium sulphate, filtered and removed on a rotary evaporator. This yielded ~4.0g of intermediate product. This was dissolved in a minimum of acetic acid. The solution was then poured into a KPF₆ solution (2g in 65ml water). This appeared to yield a viscous liquid. This was extracted with dichloromethane. The dichloromethane layer was washed with 3x100ml water and then dried with magnesium sulphate, and the solvent was removed on a rotary evaporator to yield the product

Product yield 2.31g (53.8%) of a brown solid.

The product was analysed by HPLC, LC-MS and IR

EXAMPLE 16

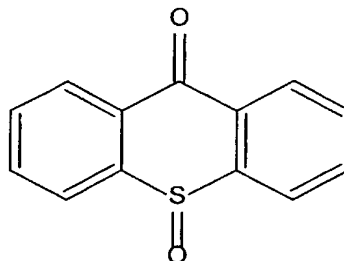
(2.025g, 0.0075moles), 2-isopropylthioxanthone sulphoxide from Example 5, 4-hydroxybiphenyl (1.768g, 0.01040moles), acetic acid (7ml), dichloromethane (1.75ml) and acetic anhydride (7ml) were mixed in a round bottomed flask. The temperature of the mixture was reduced to <15°C using a water/ice bath. Concentrated sulphuric acid (2.6ml) was then added drop wise, making sure the temperature did not exceed 15°C. After the addition was complete, the mixture was stirred for 2 hours, allowing the temperature to increase to room temperature. 100ml of water was then added to the mixture. This was then extracted with ~200ml (2x100ml) of dichloromethane. The dichloromethane was then removed on a rotary evaporator. This yielded 5.91g of intermediate product. This was dissolved in a minimum of acetic acid. The solution was then poured into a KPF₆ solution (2.5g in 75ml water). This appeared to yield a viscous liquid. This was extracted with dichloromethane. The dichloromethane layer was then dried with magnesium sulphate and the solvent was removed on a rotary evaporator to yield the product. A second extraction was carried out to purify the product further as there was still a strong odour of acetic acid.

Product is a brown solid, yield not recorded

The product was analysed by HPLC, LC-MS and IR. Analysis suggests product is a mixture of hydroxy and acetyl biphenyl derivatives (produced under the conditions of the reaction).

COMPARATIVE EXAMPLE 1

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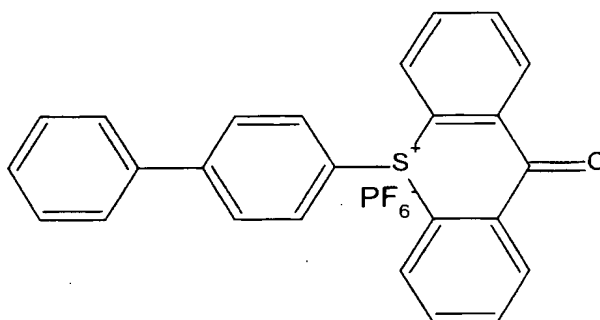
8.35g of Thioxanthone (0.03937moles) were dissolved in 630ml of a mixture of acetonitrile and water (75% acetonitrile, 25% water). A further 75ml of acetonitrile was added in an unsuccessful attempt to dissolve the thioxanthone. The mixture was heated to 55°C. 86.336g of Ceric ammonium nitrate (0.15748moles) was added, and the reaction was carried out, followed by thin layer chromatography (TLC). The reaction mixture was stirred for 90mins at 55°C. 400ml of water was then added which, when cooled, resulted in the product crystallising from solution. The crystals were remove by filtration and then dried in a vacuum oven.

15 Product yield 7.23g (80.54%) of a yellow solid.

The product was analysed by HPLC, LC-MS and IR

COMPARATIVE EXAMPLE 2

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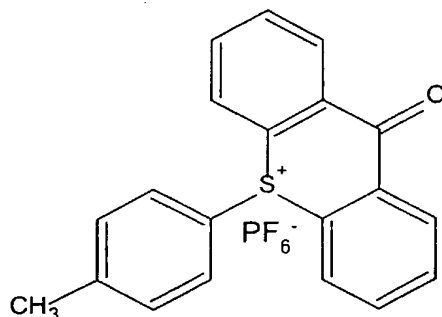
1.71g (0.0075moles) of thioxanthone sulfoxide from Comparative Example 1, 1.604g biphenyl (0.01040moles), acetic acid (7ml), dichloromethane (1.75ml) and acetic anhydride (7ml) were mixed in a round bottomed flask. The temperature of the mixture was reduced to <15°C using a water/ice bath. Concentrated sulphuric acid (2.6ml) was then added drop wise, making sure the temperature did not exceed 15°C. After the addition was complete, the mixture was stirred for 2 hours, allowing the temperature to increase to room temperature. 100ml of water was then added to the mixture. This was then extracted with ~200ml (2x100ml) of dichloromethane. The dichloromethane was then removed on a rotary evaporator to give 5.17g of intermediate product. This was dissolved in a minimum of acetic acid. The solution was then poured into a KPF₆ solution (2.5g in 75ml water). The product crystallised from solution and was collected by filtration, washed with water and then dried in a vacuum oven.

Product yield 2.38g (62.2%) of a brown solid.

The product was analysed by HPLC, LC-MS and IR

COMPARATIVE EXAMPLE 3 (ATTEMPTED SYNTHESIS)

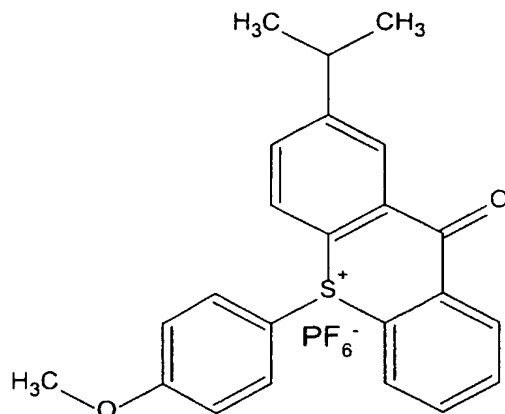
5



1.71g (0.0075moles) of thioxanthone sulfoxide from Comparative Example 1, 0.96g toluene (0.01040moles), acetic acid (7ml), dichloromethane (1.75ml) and acetic anhydride (7ml) were mixed
10 in a round bottomed flask. The temperature of the mixture was reduced to <15°C using a water/ice bath. Concentrated sulphuric acid (2.6ml) was then added drop wise, making sure the temperature did not exceed 15°C. After the addition was complete, the mixture was stirred for 2 hours, allowing the temperature to increase to room temperature. 100ml of water was then added to the mixture. This was then extracted with ~200ml (2x100ml) of dichloromethane. The dichloromethane was then
15 removed on a rotary evaporator to give 1.51g of intermediate product. This was dissolved in a minimum of acetic acid. The solution was then poured into a KPF₆ solution (2g in 65ml water). The product crystallised from solution and was collected by filtration, washed with water and then dried in a vacuum oven.

Product yield 0.48g of a brown solid.

20 The product was analysed by HPLC, LC-MS and IR and found not to have produced any product. Analysis suggests the isolated product is still the thioxanthone sulfoxide starting material.

COMPARATIVE EXAMPLE 4

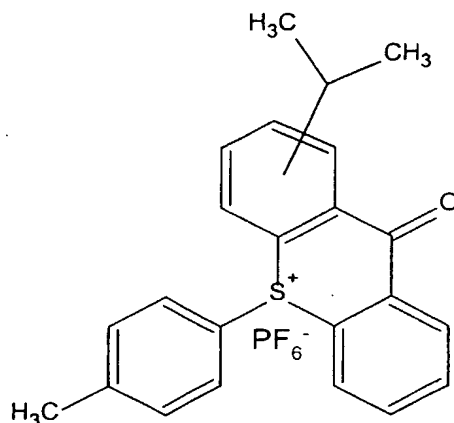
Isopropylthioxanthone sulphoxide (2.025g, 0.0075moles) from Comparative Example 1, anisole (1.1232g, 0.01040moles), acetic acid (7ml), dichloromethane (1.75ml) and acetic anhydride (7ml) were mixed in a round bottomed flask. The temperature of the mixture was reduced to <15°C using a water/ice bath. Concentrated sulphuric acid (2.6ml) was then added drop wise, making sure the temperature did not exceed 15°C. After the addition was complete, the mixture was stirred for 2 hours, allowing the temperature to increase to room temperature. 100ml of water was then added to the mixture. This was then extracted with ~200ml (2x100ml) of dichloromethane. The dichloromethane was then removed on a rotary evaporator. This yielded 10.0g of intermediate product. This was dissolved in a minimum of acetic acid. The solution was then poured into a KPF₆ solution (4g in 130ml water). This appeared to yield a viscous liquid. This was extracted with dichloromethane. The dichloromethane layer was then dried with magnesium sulphate, and the solvent was removed on a rotary evaporator to yield the product.

Product yield 2.88g (75.9%) of a brown viscous liquid.

The product was analysed by HPLC, LC-MS and IR

COMPARATIVE EXAMPLE 5

5



Isopropylthioxanthone sulphoxide (2.025g, 0.0075moles) from Comparative Example 1,
10 toluene (0.9568g, 0.01040moles), acetic acid (7ml), dichloromethane (1.75ml) and acetic anhydride
(7ml) were mixed in a round bottomed flask. The temperature of the mixture was reduced to <15°C
using a water/ice bath. Concentrated sulphuric acid (2.6ml) was then added drop wise, making sure
the temperature did not exceed 15°C. After the addition was complete, the mixture was stirred for 2
hours, allowing the temperature to increase to room temperature. 100ml of water was then added to
15 the mixture. This was then extracted with ~200ml (2x100ml) of dichloromethane. The
dichloromethane was then dried with magnesium sulphate and the dichloromethane then removed on a
rotary evaporator. This yielded 2.72g of intermediate product. This was dissolved in a minimum of
acetic acid. The solution was then poured into a KPF₆ solution (2g in 65ml water). This appeared to
yield a viscous liquid. This was extracted with dichloromethane. The dichloromethane layer was then
20 dried with magnesium sulphate and the solvent was removed on a rotary evaporator to yield the
product.

Product yield 2.28g (62.04%) of a brown viscous liquid.

The product was analysed by HPLC, LC-MS and IR.

EXAMPLE 17**Varnish Formulations.**

The following varnish formulations were used in the evaluation experiments.

Material Code/ Description	Standard Varnish 1	Standard Varnish 2	Experimental Varnish 1	Experimental Varnish 2
Uvacure 1500	91.8	87.8	95.8	91.8
Tegorad 2100	0.2	0.2	0.2	0.2
Propylene carbonate	-	4.0	-	4.0
Uvacure 1592*	8.0	8.0	-	-
Experimental Photoinitiator	-	-	4.0	4.0
Total	100.0	100.0	100.0	100.0

Uvacure 1592 is a standard photoinitiator from UCB (supplied as a 50% solution in propylene carbonate.)

Uvacure 1500 is a cycloaliphatic epoxide monomer from UCB.

Tegorad 2100 is a wetting aid from TEGO.

Summary of Curing Experiments.

The varnishes were printed onto Leneta opacity charts using a No.1 K-bar and draw down pad. The prints were passed through a UV curing rig fitted with a medium pressure mercury arc lamp at 80m/min. The UV lamp power is 280watts/inch.

- 5 Standard Varnish formulations 1 & 2, containing the photoinitiator Uvacure 1592 cure with one pass at the UV rig conditions stated above. However, the photoinitiator Uvacure 1592 is only completely soluble with additional propylene carbonate (Standard Varnish formulation 2). Colour on cure is good but there is a very strong diphenyl sulphide odour.

Initiator Code	Initiator Description	Soluble	Curing Results Summary			
			Number of passes to cure		Odour	Colour of film
			Experimental varnish 1 (No propylene carbonate)	Experimental varnish 2 (4% propylene carbonate)		
Comparative Example 5	ITX / Toluene	Yes	>15	9	No	Slightly Yellow
Comparative Example 4	ITX / Anisole	Yes	10	2-3	No	Slightly Yellow
Example 2	ITX / Biphenyl	Yes	1	1	No	Slightly Yellow
Comparative Example 2	TX / Biphenyl	No	1	1	No	Slightly Yellow
Example 8	CTX / Biphenyl	No	1-2	1	No	Slightly Yellow
Example 6	2-ITX / Biphenyl	Yes	1	1	No	Slightly Yellow
Example 4	DETX / Biphenyl	Yes	1	1	No	Slightly Yellow
Example 13	Dibenzo-thiophene / Biphenyl	No	1-2	1	No	None
Example 12	2-ITX / 4-Methyl-biphenyl	Yes	2	1	No	Slightly Yellow
Example 16	2-ITX / 4-Hydroxy-biphenyl	Yes	>6	2-3	No	Slightly Yellow
Example 11	2-ITX / Diphenyl ether	Yes	1	1	No	Slightly Yellow
Example 10	CPTX / Biphenyl	No	>7	2	No	Very Yellow
Example 14	Thianthrene / Biphenyl	Yes	1	1	No	None
Example 15	DETX / Fluorene	No	3	2-3	No	Slightly Yellow

EXAMPLE 18**5 Evaluation results for Example 6 in UV flexo inks****Ink formulation.**

Ingredient	Yellow test	Yellow Std	Magenta Test	Magenta Std	Cyan Test	Cyan Std	Black Test	Black Std
Pigment Concentrate	44.0	44.0	56.8	56.8	54.0	54.0	70.0	70.0
TMPO	39.6	39.6	30.3	30.3	33.0	33.0	22.0	22.0
Uvacure 1500	8.4	8.4	4.9	4.9	4.7	4.7	-	-
Uvacure 1592	8.0	-	8.0	-	8.0	-	8.0	-
Example 6 (50% solids in Uvacure 1500)	-	8.0	-	8.0	-	8.0	-	8.0

Uvacure 1592, a triaryl sulphonium salt photoinitiator from UCB, was supplied at 50% solids
 10 in propylene carbonate.

TMPO is trimethylolpropane oxetane from Perstorp

Cure and Test conditions

The inks were printed on SWH-30, BOPP film from Hoechst, using the Easiproof hand held
 flexo proofer with anilox tool 41. The prints were cured under a medium pressure mercury arc lamp at
 15 a belt speed of 80m/min with a lamp power of 120W/cm.

The inks were assessed for MEK resistance, scratch, thumb twist and adhesion. The MEK
 resistance was assessed immediately after cure and 3 days later. The test ink and the standard were
 printed side-by-side and alone.

Cure results.

20 All formulations were found to cure with a single pass under the UV lamp with the conditions
 described.

Yellow

Printing conditions	Ink	MEK		Scratch	Thumb Twist	Adhesion
		Immediate	3 Days			
Side by side	Std	23	62	✓	✓	100%
	Test	10	35	✓	✓	100%
Alone	Std	6	31	✓	✓	100%
	Test	6	24	✓	✓	100%

5

Magenta

Printing conditions	Ink	MEK		Scratch	Thumb Twist	Adhesion
		Immediate	3 Days			
Side by side	Std	2	32	✓	✓	100%
	Test	5	17	Inferior, As std after 90s	✓	100%
Alone	Std	6	17	✓	✓	100%
	Test	2	12	Inferior, As std after 90s	Inferior, as std after 30s	100%

Cyan

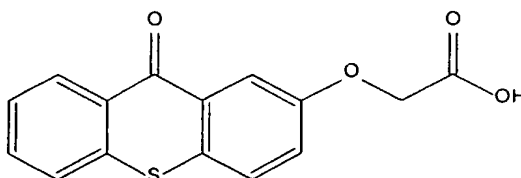
Printing conditions	Ink	MEK		Scratch	Thumb Twist	Adhesion
		Immediate	3 Days			
Side by side	Std	3	na	✓	✓	100
	Test	2	na	✓	✓	100
Alone	Std	4	na	✓	✓	100% (Slow) 0% jerky
	Test	2	na	✓	✓	100

Black

Printing conditions	Ink	MEK		Scratch	Thumb Twist	Adhesion
		Immediate	3 Days			
Side by side	Std	3	21	✓	✓	0%
	Test	1	9	✓	✓	0%
Alone	Std	4	21	After 30s	✓	Slow 100% Jerky 0%
	Test	2	10	After 30s	✓	Slow 100% Jerky 0%

EXAMPLE 19

5

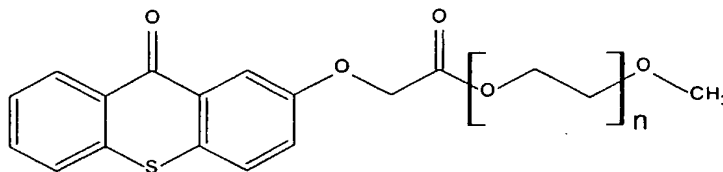


24 g sodium hydroxide was refluxed in 400 ml tetrahydrofuran for five minutes. 22.8 g (0.1
10 mols) hydroxythioxanthone was added and reflux continued for 1 hour, during which time the colour
changed to bright red, indicating the formation of the sodium salt of hydroxythioxanthone. 35.1 g
(0.21 mols) of ethyl bromoacetate was added and reflux was continued for three hours. After cooling
to room temperature, 400 ml of deionised water were added with stirring, and the tetrahydrofuran was
distilled out to yield a clear red solution. Reflux was continued for a further 2 hours in order to
15 hydrolyse all the ester intermediate. The solution was then cooled to 50°C and 400 ml 1.0 M aqueous
hydrochloric acid was added with stirring, causing the solid product to precipitate out. After refluxing
for five minutes to be sure that all the sodium salt was converted to free acid, the solution was cooled
to room temperature and stirred for two hours before filtering off the solid, washing with 400 ml
deionised water and drying in a vacuum oven at 80 °C.

20 Product yield 28.12 g (97 %). Product analysed by NMR.

EXAMPLE 20

5

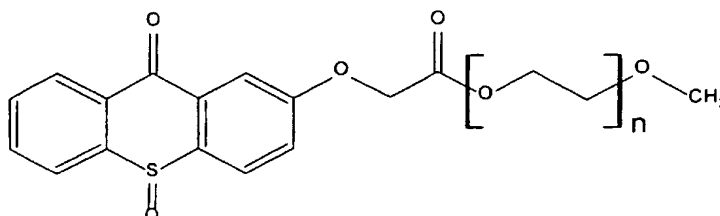


18.0 g (0.063 mols) carboxymethoxythioxanthone from Example 19 and 19.6g (0.056 mols)
10 of polyethylene glycol methyl ether (350 molecular weight) were azeotropically refluxed under nitrogen in 200 ml toluene with 0.6 g p-toluenesulphonic acid monohydrate catalyst. After 10 hours, the solution was cooled to 35 °C and washed twice with 100ml 10% aqueous potassium carbonate solution and 100 ml deionised water before drying over anhydrous magnesium sulphate. The solution was filtered and all solvent was removed on a rotary evaporator to yield an orange oil.

15 Product yield 25.47 g (73.6 %). Product analysed by HPLC and IR

EXAMPLE 21

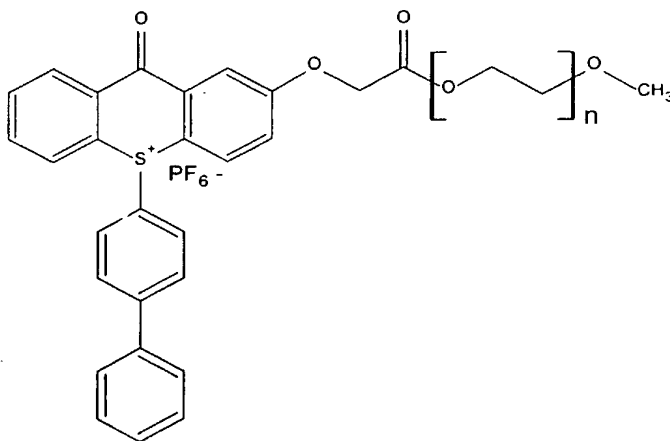
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- 10 5.0g of the product from Example 20 (0.0080906moles) were dissolved in 129.5ml of acetonitrile / water (75:25). 17.74g (0.03236moles) of CAN were added in one batch. The reaction mixture was stirred for 1 hour at room temperature. 82ml of water was then added. The mixture was then extracted with 3x50ml of dichloromethane. The organic extracts were combined and dried with magnesium sulphate and then filtered. The solvent was removed on a rotary evaporator to yield the product.
- 15 Product yield 5.00g (97.5%) of a yellow liquid. The product was analysed by FT-IR and HPLC.

EXAMPLE 22

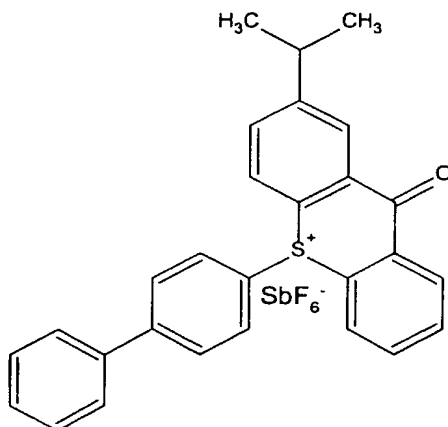
5



- 4.0g of the product from Example 21 (0.0063091 moles), biphenyl (0.972g, 0.00631 moles) and acetic anhydride (5.2ml) were mixed in a round bottomed flask. The temperature of the mixture was reduced to approx. 10°C using a water/ice bath. Conc. Sulphuric acid (1.97g) was then added drop-wise making sure that the temperature did not exceed 20°C. The mixture was then added drop-wise to a solution of 1.37g potassium hexafluoro phosphate (KPF₆) in water 8.52g / methanol 10.1g. 2ml of methanol was also used to wash out the reaction vessel and added to the methanol/water/ KPF₆ solution. The mixture was then stirred at 35-40°C for 30 minutes. The mixture was then cooled to 10°C and stirred for a further 30 minutes. No product crystallised. Therefore, 50ml of MEK and 50ml of water were added but separation did not occur. 75ml of DCM were added to extract the product and then a further 30ml of DCM. The DCM extracts were combined and dried with magnesium sulphate. The DCM was then filtered and finally removed on a rotary evaporator to yield the product.
- Product yield 5.94g of a viscous brown liquid/paste. The product was analysed by FT-IR and HPLC.

EXAMPLE 23

5



5g of the product of Example 5 (0.01852moles), biphenyl (2.852g, 0.01852moles) and acetic
10 anhydride (15.12g) were mixed in a round bottomed flask. The temperature of the mixture was
reduced to <10°C using a water/ice bath. Concentrated sulphuric acid (5.79g) was then added drop
wise, making sure the temperature did not exceed 20°C. After the addition was complete, the mixture
was added to a solution of methanol (29.5g), water (25.0g) and KSbF₆ (5.97g). The mixture was then
15 stirred at 35-40°C for 30 minutes. The mixture was then cooled to <10°C using an ice/water bath and
stirring continued for a further 30 minutes. The precipitate was collected by filtration and washed with
50ml of water. The material was then dried in the vacuum oven at 40°C for 4 hours.

Product yield 8.85g (74.34%) of a brown solid. The product was analysed by HPLC and IR.

EXAMPLE 24Varnish Formulations.

The following varnish formulations were used in the evaluation experiments.

5

Material Code/Description	Standard Varnish	Experimental Varnish
Uvacure 1500	91.8	95.8
Tegorad 2100	0.2	0.2
Propylene carbonate	-	-
Uvacure 1592	8.0	-
Experimental Photoinitiator	-	4.0
Total	100.0	100.0

Uvacure 1592 is a standard photoinitiator from UCB (supplied as a 50% solution in propylene carbonate).

Uvacure 1500 is a cycloaliphatic epoxide monomer from UCB.

10

Tegorad 2100 is a wetting aid from TEGO

Summary of Curing Experiments.

The varnishes were printed onto Leneta opacity charts using a No.0 K-bar and draw down pad. The prints were passed through a Primarc Maxicure UV curing rig fitted with a medium pressure mercury arc lamp at 80m/min. The UV lamp power is 300 Watts/inch and was run at a half power setting to aid product differentiation.

15

Initiator Code	Initiator Description	Soluble	No. passes to cure	Odour	Colour
Uvacure 1592	Standard triarylsulphon ium salt	With difficulty	1	Strong (diphenyl sulphide)	Colourless
Example 22	PEG350CMT X / Biphenyl PF ₆	Yes	2	No	Slightly Yellow
Example 23	2-ITX / Biphenyl SbF ₆	Yes	1	No	Slightly Yellow

These results demonstrate that the experimental photoinitiators of the present invention have cure speed similar to those of one of the best available commercial standard photoinitiators. Solubility and odour on cure are superior to that of the standard photoinitiator.

5

EXAMPLE 25

GC-MS headspace analysis

The following varnish formulations were used in the evaluation experiments.

Material Code / Description	Sulphonium salt formulations	Iodonium salt formulation
Uvacure 1500	75	77.5
TMPO	20.9	18.9
Tegorad 2100	0.1	0.1
Propylene carbonate	2	-
Photoinitiator	2	1.5
Esacure KIP 150	-	2

- 10 The standard photoinitiators used were Uvacure 1592 (triarylsulphonium salt photoinitiator from UCB, supplied as a 50% solution in propylene carbonate) and IGM 440 (diaryliodonium salt photoinitiator from IGM).

Uvacure 1500 is a cycloaliphatic epoxide monomer from UCB.

Tegorad 2100 is a wetting aid from TEGO.

- 15 TMPO is a monofunctional oxetane alcohol diluent from Perstorp.

Esacure KIP 150 is a hydroxyalkylphenone photoinitiator from Lamberti.

- 20 The varnishes were printed onto aluminium foil using a No.0 K-bar and draw down pad. The prints were passed twice through a Primarc Maxicure UV curing rig fitted with a 300 Watts/inch medium pressure mercury arc lamp at 80m/min. Under these conditions the samples were over-cured, which was desirable in order to maximise the amount of by-product formation. 200cm² of each sample was placed in a sealed tube and subjected to a standard headspace analysis procedure where they are heated to 200°C for 10 minutes and then the headspace volume transferred to a gas chromatograph fitted with a mass spectrometer detector via a heated transfer line.

- 25 The compounds detected in these analyses are shown below. No attempt was made to quantify individual materials. Note that there were also several peaks common to all samples that derive from the Uvacure 1500.

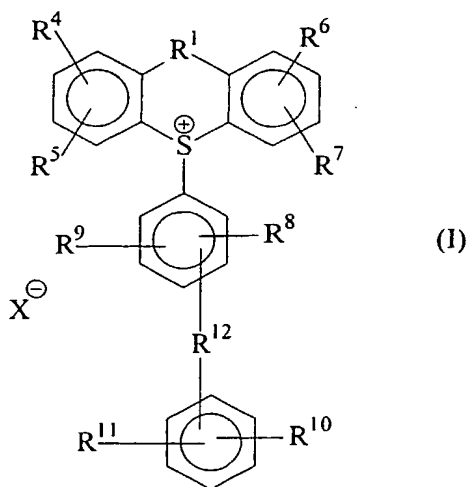
Photoinitiator	Materials detected in Head-space procedure
Uvacure 1592	Diphenyl sulphide Several small unidentified peaks *
IGM 440	Toluene Iodobenzene Several unidentified peaks
Example 6	Biphenyl

*Benzene would also be expected from this analysis but was not seen due to the solvent delay used in this standard GC method.

5 These results demonstrate that for Example 6, the only photoinitiator byproduct detected is biphenyl, which is of limited toxicological concern for food packaging inks as it is itself an approved food additive material. This is in contrast with the undesirable materials released from the 2 standard photoinitiators.

CLAIMS

1. Compounds of formula (I):



in which:

5 R^1 represents a direct bond, an oxygen atom, a group $>CH_2$, a sulphur atom, a group $>C=O$, a group $-(CH_2)_2-$ or a group of formula $-N-R^a$, where R^a represents a hydrogen atom or a C_1 - C_{12} alkyl group having from 1 to 12 carbon atoms;

R^4 , R^5 , R^6 and R^7 are independently selected from hydrogen atoms and substituents α , defined below, provided that, when R^1 represents a group $>C=O$, then at least one of R^4 , R^5 , R^6 and R^7 represents a substituent α ;

10 R^8 , R^9 , R^{10} and R^{11} are independently selected from hydrogen atoms, hydroxy groups, and C_1 - C_4 alkyl groups;

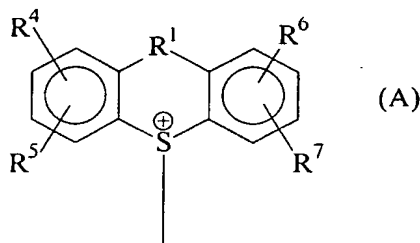
or R^9 and R^{11} are joined to form a fused ring system with the benzene rings to which they are attached;

15 R^{12} represents a direct bond, an oxygen atom or a $-CH_2-$ group;

said substituents α are: a C_1 - C_{20} alkyl group, a C_1 - C_{20} alkoxy group, a C_2 - C_{20} alkenyl group, a halogen atom, a nitrile group, a hydroxyl group, a C_6 - C_{10} aryl group, a C_7 - C_{13} aralkyl group, a C_6 - C_{10} aryloxy group, a C_7 - C_{13} aralkyloxy group, a C_8 - C_{12} arylalkenyl group, a C_3 - C_8 cycloalkyl group, a carboxy group, a C_2 - C_7 carboxyalkoxy group, a C_2 - C_7 alkoxycarbonyl group, a C_7 - C_{13} aryloxycarbonyl group, a C_2 - C_7 alkylcarbonyloxy group, a C_1 - C_6 alkanesulphonyl group, a C_6 - C_{10} arenesulphonyl group, a C_1 - C_6 alkanoyl group or a C_7 - C_{11} arylcarbonyl group; and

X^- represents an anion, provided X^- does not represent an alkoxy, hydroxyalkoxy or aryloxy group, or perchlorate group, when R^1 represents a direct bond; and esters thereof.

2. Compounds according to Claim 1, in which R^4 , R^5 , R^6 and R^7 are independently selected from hydrogen atoms, C_1 - C_{10} alkyl groups, a C_1 - C_{10} alkoxy groups, halogen atoms, and C_3 - C_8 cycloalkyl groups.
3. Compounds according to Claim 1 or Claim 2, in which three or four of R^4 , R^5 , R^6 and R^7 represent hydrogen atoms.
4. Compounds according to Claim 3, in which one or more of R^4 , R^5 , R^6 and R^7 represents an ethyl or isopropyl group.
5. Compounds according to any one of Claims 1 to 4, in which two, three or four of R^8 , R^9 , R^{10} and R^{11} represent hydrogen atoms.
6. Compounds according to any one of Claims 1 to 4, in which all of R^8 , R^9 , R^{10} and R^{11} represent hydrogen atoms.
7. Compounds according to any one of Claims 1 to 6, in which R^1 represents a group $>C=O$, a sulphur atom or a direct bond.
8. Compounds according to Claim 7, in which R^1 represents a group $>C=O$.
9. Compounds according to any one of Claims 1 to 6, in which that part of the compound of formula (I) having the formula (A):



(in which R^1 , R^4 , R^5 , R^6 and R^7 are as defined in Claim 1) is a residue of substituted or unsubstituted thianthrene, dibenzothiophene, thioxanthone, thioxanthene, phenoxathiin phenothiazine or N-alkylphenothiazine.

10. Compounds according to Claim 9, in which said residue is substituted thioxanthone.
11. Compounds according to Claim 9, in which said residue is substituted or unsubstituted thianthrene.
12. Compounds according to Claim 9, in which said residue is substituted dibenzothiophene.
13. Compounds according to Claim 9, in which said residue is substituted or unsubstituted phenoxathiin.

14. Compounds according to Claim 9, in which said residue is substituted or unsubstituted phenothiazine or N-alkylphenothiazine

15. Compounds according to any one of the preceding Claims, in which:

R^4 , R^5 , R^6 and R^7 are individually the same or different and each represents a hydrogen atom or an alkyl group having from 1 to 4 carbon atoms;

R^{12} represents a direct bond; and

R^8 , R^9 , R^{10} and R^{11} represent hydrogen atoms.

16. Compounds according to any one of the preceding Claims, in which X^- represents a PF_6^- , SbF_6^- ,

AsF_6^- , BF_4^- , $B(C_6F_5)_4^-$, $R^aB(Ph)_3^-$ (where R^a represents a C_1 - C_6 alkyl group and Ph represents a

10 phenyl group), $R^bSO_3^-$ (where R^b represents a C_1 - C_6 alkyl or haloalkyl group or an aryl group), or

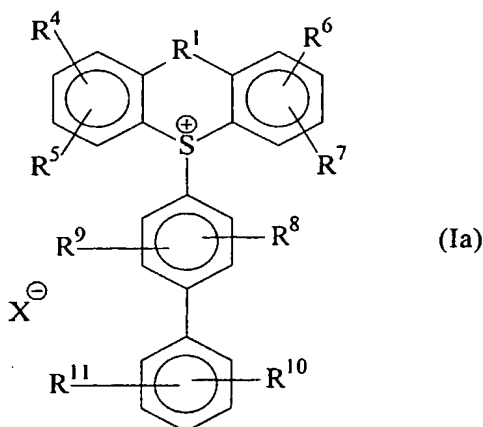
$ArSO_3^-$ (where Ar represents an aryl group) group.

17. Compounds according to Claim 16, in which X^- represents a PF_6^- , SbF_6^- , AsF_6^- , $CF_3SO_3^-$ or

BF_4^- group.

18. Compounds according to Claim 17, in which X^- represents a PF_6^- group.

15 19. Compounds according to any one of the preceding Claims, having the formula:



in which R^1 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} and X are as defined in Claim 1.

20. An energy-curable composition comprising: (a) a polymerisable monomer, prepolymer or oligomer; and (b) a photoinitiator which is a compound of formula (I), as claimed in any one of

20 Claims 1 to 19.

INTERNATIONAL SEARCH REPORT

 International Application No
 PCT/US 03/06106

A. CLASSIFICATION OF SUBJECT MATTER

 IPC 7 C07D333/76 C07D335/12 C07D335/16 C07D339/08 C07D279/20
 C09D11/10 C08F2/46

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07D C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 161 478 A (J. CRIVELLO) 17 July 1979 (1979-07-17) cited in the application the whole document ---	1,9,19, 20
A	US 5 731 364 A (R.F. SINTA ET AL.) 24 March 1998 (1998-03-24) the whole document ---	1,9,19, 20
P,X	WO 03 08404 A (LAMBERTI) 30 January 2003 (2003-01-30) page 1; claims 1,7,10,11,16 --- -/--	1,9,19, 20

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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"A" document defining the general state of the art which is not considered to be of particular relevance

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search

27 June 2003

Date of mailing of the international search report

07/07/2003

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